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(21) International Application Number: PCT/US90/05013 (22) International Filing Date: 5 September 1990 (05.09.90) (30) Priority data: 404,642 8 September 1989 (08.09.89) US (71) Applicant: DESOTO, INC. [US/US]; 1700 South Mount Prospect Road, Des Plaines, IL 60017 (US). (72) Inventors: VANDEBERG, John, T. ; 415 West Oakwood Drive, Barrington, IL 60010 (US). MURRAY, Kevin, P. ; 1759 Glen Lake Road, Hoffman Estates, IL 60195 (US). KRAJEWSKI, John, J. ; 932 Valley Stream, Wheeling, IL 60090 (US). ZIMMERMAN, John, M. ; 4450 Shorewood Drive, Hoffman Estates, IL 60195 (US).		(74) Agents: KATZ, Martin, L.; Dressler, Goldsmith, Shore, Sutker & Milnamow, Ltd., 180 North Stetson Street, Two Prudential Plaza, Suite 4700, Chicago, IL 60601 (US) et al. (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMERIZABLE OLIGOMERS AND COATINGS BASED ON BUTADIENE (57) Abstract A polymerizable ethylenically unsaturated oligomer which is a reaction product of: (1) a polybutadiene oligomer carrying two reactive groups and lacking significant unsaturation, the oligomer containing at least about 60 % by weight of butadiene polymerized in the 1,2 position with the balance of the butadiene polymerized in the 1,4 position, said difunctional oligomer having a number average molecular weight of from about 500 to about 5,000 daltons and (2) a monofunctional ethylenically unsaturated compound, the unsaturated oligomer having a number average molecular weight of from about 1,000 to about 10,000 and containing at least about 40 % by weight of the polybutadiene oligomer. These unsaturated oligomers are combined with an ethylenically unsaturated liquid comprising alkyl (meth)acrylate to form cured coatings having superior resistance to water.		

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"POLYMERIZABLE OLIGOMERS AND COATINGS BASED ON
BUTADIENE"

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DESCRIPTION

Technical Field

10 This invention relates to photopolymerizable
ethylenically unsaturated oligomers based on saturated
butadiene oligomers having a pair of reactive groups,
preferably diols having a high 1,2-butylene content.
While unsaturated oligomers of various type are
contemplated, unsaturated polyurethanes, which can
15 contain urea groups, are preferred, especially for
application to optical glass fibers. The unsaturation
which is contemplated is preferably (meth)acrylate
unsaturation or an admixture of vinyl ether groups and
ethylenically unsaturated dicarboxylates, preferably
maleates or fumarates. The unsaturated oligomers can be
20 cured by exposure to energy, e.g., light, in the
presence of a photoinitiator or electrons from an
electron beam in the absence of a photoinitiator.

Background Art

25 Ethylenically unsaturated polyurethane
oligomers are known to be employed in photocurable
compositions which are to be used in the coating of
optical glass fibers. One of the problems encountered
in the use of the known compositions is the moisture
sensitivity of the cured coatings which leads to various
30 difficulties including loss of adhesion upon exposure to
moisture. Other difficulties are inadequate thermal
stability and inadequate hydrolytic stability. It is
desirable to reduce the moisture sensitivity of the
cured coatings while maintaining resistance to
35 embrittlement at low service temperatures, but this is

therefrom, and having a number average molecular weight of from about 500 to about 5,000 daltons;

5 (2) a molar excess of an organic compound having a plurality of groups reactive with the reactive groups of the oligomer, e.g., the hydroxy groups of the oligomer diol, to provide reactive terminal groups; and

10 (3) a monofunctional ethylenically unsaturated compound, preferably a (meth)acrylate which is reactive directly with the reactive groups of the polybutadiene oligomer or with the reactive terminal groups of (2). In place of the (meth)acrylate one can use other monofunctional ethylenically unsaturated compounds, or mixtures thereof, such as a monofunctional vinyl ether or a monofunctional ethylenically unsaturated
15 carboxylate, preferably a maleate or fumarate. Since the oligomer is preferably a diol, the monofunctionality of the unsaturated compound is preferably constituted by a single hydroxy group.

20 The ethylenically unsaturated oligomer which is produced has a number average molecular weight of from about 1,000 to about 10,000, preferably about 1,500 to about 5,000, daltons, and it contains at least about 40% by weight of the polybutadiene oligomer.

25 It is desired to stress that component (2) above is optional where the monofunctionality of component (3) is directly reactive with the two reactive groups in the oligomer, as by esterification. On the other hand, it is preferred to employ oligomer diols and to react those diols with anhydrides, such as
30 diisocyanates or diepoxides, so as to ease the burden of reaction and thus obtain a substantially complete reaction while avoiding undesired side reactions.

35 The unsaturation in the polybutadiene oligomer, i.e., (1), must be consumed to an extent that the residual unsaturation no longer disturbs the

As will be evident, the two described reactions can be carried out simultaneously or sequentially and both of these variations are intended to be embraced by reference to a reaction product involving the various reactants.

The polybutadiene oligomer diols which are used herein are made by anionic polymerization and are available in commerce. A preferred commercial product useful herein can be obtained from Nippon Soda Corporation, Ltd. of Tokyo, Japan, under the trade designation Nisso PB GI 1000. This product is a hydrogen-saturated polybutadiene diol having about 85% branched butylene groups formed by a 1,2-polymerization and 15% butylene groups formed by a 1,4-polymerization and a number average molecular weight of about 1,000 daltons. Corresponding products having a number average molecular weight of about 2,000 and 3,000 daltons are also available.

As will be understood, while the preferred difunctional polybutadiene oligomers are hydroxy functional, the hydroxy groups can be replaced by other reactive groups, such as carboxyl groups, mercapto groups, amino groups, and the like. These other reactive groups can be employed in place of the hydroxy group to form ethylenically unsaturated derivatives in much the same way as the oligomer diol. Thus, the diol can be reacted with a diisocyanate and hydroxyethyl acrylate. The oligomer dimercaptan can replace the oligomer diol. Similarly, the oligomer diol can be reacted with acrylic acid to form the unsaturated derivative by ester formation. One can reverse this by esterifying the oligomer dicarboxylate with hydroxyethyl acrylate.

The unsaturated oligomers which have been described can be incorporated into photocurable and

The difunctional polybutadiene oligomers of the present invention are also useful to prepare cable structures including ribbon materials wherein coated fibers are bound together with a cured coating composition of the present invention.

All proportions and percentages herein are by weight, unless otherwise stated, and molecular weights, as is conventional, are reported in daltons.

The term "dalton", as used herein in its various grammatical forms, defines a unit of mass that is 1/12th the mass of carbon-12.

The compositions of the present invention are curable by exposure to ultraviolet light when a photoinitiator, including visible light near the ultraviolet range. Appropriate wavelengths will be discussed hereinafter.

Photoinitiators include aryl ketones and are sometimes added to the composition shortly before use. When the monoethylenically unsaturated compound comprises a vinyl ether and a maleate or fumarate, the preferred photoinitiator is selected from the group consisting of hydroxy or alkoxy-functional acetophenone derivatives and benzoyl diaryl phosphine oxides.

The present compositions are also curable by exposure to electrons from an electron beam in the absence of a photoinitiator.

The polybutadiene oligomer can be an acrylate-terminated polyurethane containing the polybutadiene diol. This polyurethane can be made by reacting polybutadiene diol with an organic diisocyanate and a monohydric acrylate, in any order.

The organic diisocyanates are well known and are illustrated by toluene diisocyanate and isophorone diisocyanate which are two of the more frequently used compounds within this well known class. The urethane

using hydroxy functional esters of maleic or fumaric acid, such as hydroxypropyl butyl maleate or fumarate.

As will be evident, the hydroxy groups in the above described illustration of this invention can be replaced by any group that is reactive with the functional group of the polyfunctional compound or the reactive groups of the polybutadiene oligomer.

When a polyepoxide, such as a diepoxide, is used as the organic compound and reacted with the diol, the reaction product is an alpha-hydroxy ether instead of a urethane. This reaction can be carried out in the presence of a Lewis acid catalyst by heating to reaction temperature which is conveniently in the range of 100° to 120° C. After removal or neutralization of the Lewis acid, the terminal epoxy-groups provided by the molar excess of polyepoxide are then reacted with a monofunctional unsaturated compound, typically acrylic acid or methacrylic acid. The reaction with these acids is a simple esterification reaction which can also be carried out without catalyst, albeit a trace of a tertiary amine or a quaternary ammonium salt will facilitate the esterification. One can also rely upon the acidity remaining from the first stage of the reaction.

The reactions of the epoxy group with hydroxy and carboxyl functionality are themselves well known, as illustrated hereinafter.

Diepoxides based on bisphenol A, such as the diglycidyl ether of bisphenol A supplied by Shell Chemical Company under the trade designation Epon 828 which has a number average molecular weight of about 390 daltons, are particularly preferred because they form hard and water-resistant reaction products having good heat resistance.

The ethylenically unsaturated liquids which are used herein preferably include a long chain alkyl (meth)acrylate, preferably one having at least carbon atoms in the alkyl group. These long chain alkyl groups normally do not exceed about 20 carbon atoms. Long chain acrylates are poorly compatible with the polyether polyurethanes utilized in the prior art, but they are excellently compatible with the unsaturated oligomers provided herein.

As a result of the enhanced capacity to tolerate long chain acrylates, photopolymerizable coatings possessing superior insensitivity to water as a result of both the selection of the unsaturated oligomer and the selection of the unsaturated monomer used to provide coating viscosity are provided by this invention. This is of particular importance in primary coatings where the usual monomers employed to soften and flexibilize the oligomers are polyethers. This is why the primary coatings now in use possess inadequate water and/or thermal resistance.

The term "liquid", and any other term used herein to describe the physical condition of anything, is used in its normal sense to denote the condition at room temperature (20° to about 30° C).

It is known that primary coatings for optical glass fibers must have great softness (low modulus and low glass transition temperature) in order to adequately resist low temperature microbending. On this basis the modulus of the cured coating should be below about 3.0 Megapascals and its glass transition temperature (T_g) should be below about 20° C. Industry now prefers the modulus to be in the range of from 1.0 to 1.5 megapascals with a (T_g) below about -12° C, and this difficult standard can be satisfied by this invention.

monovinyl ether, then the polymaleates or polyfumarates used to help cure that oligomer should contain hydrocarbon groups having at least 6 carbon atoms. The use of the vinyl ether group in combination with a maleate or fumarate results in increased cure speed which is desirable.

While useful results are obtained without a precise balance between the vinyl ether groups and the maleate or fumarate groups, the fastest and best cures are obtained when these two groups are present in about stoichiometric proportions, i.e., about 1:1. Thus, the cure speed falls off badly when the equivalent ratio of the two types of groups is outside the range of about 5:1 to about 1:5, preferably 2:1 to 1:2.

These two separate functionalities may be present in the same oligomeric molecule, i.e., the vinyl ether compound and the ester can be present in the same oligomeric molecule.

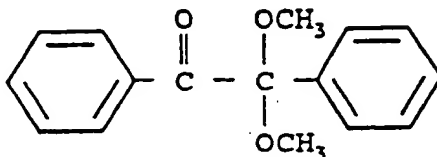
To illustrate an oligomeric molecule having the two types of unsaturations one may provide the vinyl ether group in a compound such as hydroxybutyl vinyl ether. Maleic anhydride can be adducted with butyl alcohol to form monobutyl maleate which is then adducted with a molar proportion of propylene oxide to form 2-hydroxypropyl monobutyl maleate. One mole of hydroxybutyl vinyl ether and one mole of 2-hydroxypropyl monobutyl maleate can then be reacted with one mole of a conventional organic diisocyanate, like isophorone diisocyanate. This reaction is preferably carried out in two stages so that all of one of the two unsaturated compounds bonds with the more reactive isocyanate group on the diisocyanate, and then the second unsaturated compound is added to react with the remaining isocyanate group. The result is a polyurethane formed in conventional manner using catalysts such as dibutyl tin

15

available compound is the Ciba-Geigy product Irgacure 651 which has the formula:

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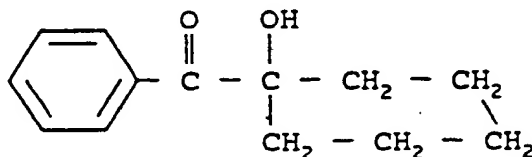
(II)



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Irgacure 184, also from Ciba-Geigy, is another useful acetophenone derivative, and it has the formula:

(III)

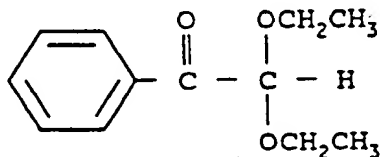


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Still another commercially available useful acetophenone derivative is diethoxy acetophenone, available from Aldrich Chemical Company, Inc. Milwaukee, Wisconsin, which has the formula:

20

(IV)

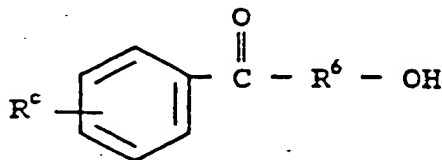


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When the photoinitiator is a hydroxy-functional compound, one can define the useful acetophenone derivatives in a somewhat different manner. Thus, the hydroxyalkyl phenones which are preferred herein have the formula:

30

(V)



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In formula VII, each R^e is independently an optional hydrocarbon substituent containing from 1 to 10 carbon atoms and which may be alkyl or aryl as previously noted, and each n is independently an integer from 1 to 3. In preferred practice, a 2,4,6-trimethyl benzoyl compound is used, and the two aromatic groups connected to the phosphorus atom are phenyl groups. This provides the compound 2,4,6-trimethyl benzoyl diphenyl phosphine oxide which is available from BASF under the trade designation Lucirin. When it is desired to harden the cured coatings, this can be achieved by employing polyacrylates, like trimethylol propane triacrylate or epoxy resin diacrylates, or high T_g monoethylenic monomers, like N-vinyl pyrrolidone, N-vinyl caprolactam, isobornyl acrylate or methyl acrylate. These are used in combination with the previously described long chain alkyl acrylates in order to minimize water sensitivity.

Referring more particularly to the light which is used for cure, its wavelength can vary somewhat depending upon the photoinitiators which are used. In present practice, the light used is usually in the ultraviolet range which extends from about 200 nanometers to about 400 nanometers. However, light of longer wavelength can be used up to about 600 nanometers, preferably up to about 520 nanometers. The photoinitiators are normally present in an amount of from 0.5% to 10%, preferably from about 2% to 6%. Representative photoinitiators are aryl ketones, such as benzophenone, acetophenone, diethoxy acetophenone, benzoin, benzil, anthraquinone, and the like. The photoinitiator may be bound to a polymer, if desired. The aforementioned acetophenone derivatives and phosphine oxides are preferred when both a vinyl ether and maleate or fumarate are utilized.

in conventional fashion using added isooctyl acrylate to control the viscosity and a temperature of about 60° C in the presence of about 0.1 percent by weight of dibutyl tin dilaurate to speed the formation of urethane groups. The reaction is carried to completion, as indicated by the elimination of isocyanate functionality.

Photocured coatings containing the above oligomer together with enough additional octyl/decyl acrylate (a commercial mixture containing the two) to provide a coating viscosity of about 4600 centipoises are soft and characterized by unusually low moisture sensitivity and high hydrolytic and oxidative stability. 4% by weight of Irgacure 184, as described previously, is used as photoinitiator and the cure is obtained with about 1 Joule per square centimeter of ultraviolet light.

Unless otherwise specified, in the following Examples the amount of photoinitiator utilized was 4% by weight, the photoinitiator utilized was Irgacure 184 and the dosage of ultraviolet light utilized was about 1 Joule per square centimeter.

Example 2

2 moles of Nisso PB GI 1000 are reacted with 4 moles of 2,2,4-trimethyl hexamethylene diisocyanate and 2 moles of 2-hydroxyethyl acrylate and 1 mole of polyoxypropylene diamine having a number average molecular weight of about 230 daltons to provide chain extension via the formation of urea groups. The reaction is carried out in conventional fashion using a temperature of about 60 degrees C in the presence of about 0.1% by weight of dibutyl tin dilaurate to speed the urethane and urea forming reactions.

Photocured coatings containing the above oligomer together with enough additional octyl/decyl

as the photoinitiator in an amount of 4% and 0.5% of Tinuvin 770 (a hindered amine light stabilizer) and 0.5% of Irganox 1035 (a hindered phenolic antioxidant) are added. These last two components are supplied by Ciba-Geigy Corporation.

Example 4

1 mole of Nisso PB GI 1000 is reacted with 2 moles of phthalic anhydride and with 2 moles of the diepoxide Epon 828 which is a diglycidyl ether of bisphenol A having a number average molecular weight of about 390 daltons, the Epon 828 having been capped with 2 moles of acrylic acid or with 2 moles of carboxyethyl acrylate. The use of phthalic anhydride reduces the tendency toward gelation encountered in Example 3.

Photocured coatings containing the above oligomer in admixture with the same monomers as in Example 3 are similar to those obtained in Example 3. The products exhibit good hydrolytic and high oxidative stability and are very insensitive to water.

Example 5

1 mole of Nisso PB GI 1000 is reacted with 2 moles of maleic anhydride and the resulting carboxyl-functional diester is reacted with 2 moles of hydroxybutyl vinyl ether. The reactions are conventional esterification reactions.

Photocured coatings containing the above oligomer are similar to those obtained in Example 3. The combination of maleic unsaturation and vinyl ether unsaturation photocures rapidly in the presence of photoinitiators of the character of Darocur 1173.

Example 6

2 moles of Nisso PB GI 1000 are reacted with 2 moles of phthalic anhydride and the addition reaction product so-obtained is combined with 3 moles of acrylic

acid and the mixture reacted with 1 mole of the epoxy cresol novolac resin ECN 1299.

5 Photocured coatings containing the above polyfunctional oligomer are similar to those obtained in Example 3, except the oligomers can vary in their physical character from low to high modulus depending on the ratio of carboxyl to hydroxyl to acrylic acid used. The water sensitivity is uniformly low.

WHAT IS CLAIMED IS:

1. A polymerizable ethylenically unsaturated oligomer which is an oligomeric ethylenically unsaturated reaction product of components comprising:

5 (1) a polybutadiene oligomer carrying two reactive groups and lacking significant unsaturation, said oligomer containing at least about 60% by weight of butadiene polymerized in the 1,2-position with the balance of the butadiene polymerized in the 1,4-position and said oligomer being hydrogenated to remove much of
10 the residual unsaturation therefrom and having a number average molecular weight of from about 500 to about 5,000 daltons; and

15 (2) a monofunctional ethylenically unsaturated compound, said unsaturated oligomer having a number average molecular weight of from about 1,000 to about 10,000 daltons and containing at least about 40% by weight of said polybutadiene oligomer.

20 2. A polymerizable ethylenically unsaturated oligomer which is an oligomeric ethylenically unsaturated reaction product of components comprising:

25 (1) a polybutadiene oligomer carrying two reactive groups and lacking significant unsaturation, said oligomer containing at least about 60% by weight of butadiene polymerized in the 1,2-position with the balance of the butadiene polymerized in the 1,4-position and said oligomer being hydrogenated to remove much of the residual unsaturation therefrom and having a number
30 average molecular weight of from about 500 to about 5,000 daltons;

(2) a molar excess of an organic compound having a plurality of groups reactive with the two functional groups of said difunctional oligomer to provide reactive terminal groups; and

9. An unsaturated oligomer as recited in claim 7 in which said difunctional organic compound is an anhydride.

5 10. An unsaturated oligomer as recited in claim 9 in which said difunctional compound is a dicarboxylic acid anhydride and said monofunctional (meth)acrylate is a monohydric acrylate.

10 11. An unsaturated oligomer as recited in claim 9 in which said difunctional compound is a diepoxide and said monofunctional (meth)acrylate is a monocarboxylic acid.

12. An unsaturated oligomer as recited in claim 11 in which said monocarboxylic acid is acrylic acid.

15 13. A polymerizable composition comprising the unsaturated oligomer of claim 1 in compatible admixture with sufficient ethylenically unsaturated liquid to provide coating viscosity, said ethylenically unsaturated liquid comprising an alkyl (meth)acrylate in which the alkyl group contains at least 6 carbon atoms.

20 14. A polymerizable composition as recited in claim 13 in which said alkyl group contains 8 to 12 carbon atoms, the monofunctional compound comprises a vinyl ether and a maleate or fumarate and the composition further comprises a photoinitiator selected from the group consisting of hydroxy- or alkoxy-functional acetophenone derivatives and benzoyl diaryl phosphine oxides.

25 15. A polymerizable composition as recited in claim 13 in which said polybutadiene oligomer is a diol and is reacted with an organic diisocyanate and a monohydric acrylate.

30 16. A polymerizable composition as recited in claim 15 in which said composition contains at least 50% of said unsaturated oligomer.

35

butadiene polymerized in the 1,2-position with the balance of the butadiene polymerized in the 1,4-position, said oligomer being hydrogenated to remove much of the residual unsaturation therefrom having a number average molecular weight of from about 500 to about 5,000 daltons;

(2) an ethylenically unsaturated compound selected from the group consisting of (meth)acrylates and monofunctional vinyl ethers, maleates or fumarate; said unsaturated oligomer having a number average molecular weight of from about 1,000 to about 10,000 daltons and containing at least about 40% by weight of said polybutadiene oligomer.

27. The unsaturated oligomer in accordance with claim 26 further comprising a photoinitiator selected from the group consisting of hydroxy- or alkoxy-functional acetophenone derivatives and benzoyl-diaryl phosphine oxides.

28. A polymerizable ethylenically unsaturated oligomer which is an oligomeric ethylenically unsaturated reaction product of components comprising:

(1) a polybutadiene oligomer having two reactive groups and lacking significant unsaturation, said oligomer containing at least about 60% by weight of butadiene polymerized in the 1,2-position with the balance of the butadiene polymerized in the 1,4-position and said oligomer being hydrogenated to remove much of the residual unsaturation therefrom and having a number average molecular weight of from about 500 to about 5,000 daltons;

(2) a monofunctional ethylenically unsaturated compound selected from the group consisting of (meth)acrylates and vinyl ether, maleate or fumarate which is reactive with the said reactive terminal groups; and said unsaturated oligomer having a number

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/05013

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 4

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08F 8/14, 8/30, 36/06, 236/06; C08L 75/16

U.S. CL. 522/102; 525/107, 123; 428/392

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System

Classification Symbols

U.S.

522/102; 525/107, 123; 428/392

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	US, A, 4,572,610 (KRAJEWSKI) 25 FEBRUARY 1986; See column 2, lines 42-44 and 20-38, column 1, lines 62-65 and column 3, lines 59-63.	1-9, 13, 21-29
Y	US, A, 4,237,245 (HALASA ET AL) 02 DECEMBER 1980; See column 2, lines 19-20 and 28-39.	1-29
Y	JP, A, 60-171248 (YOSHIRHARA ET AL) 04 SEPTEMBER 1985; See pages 5-8 of PTO translation PTO 90-2248.	1-29
Y	JP, A, 55-152712 (SUZUKI ET AL) 28 NOVEMBER 1980; See pages 5-8 of PTO translation PTO 90-2250.	1-29
Y	US, A, 4,177,074 (PROSKOW) 04 DECEMBER 1979 See columns 2 and 3.	1-29

* Special categories of cited documents: 10

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invention

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cannot be considered novel or cannot be considered to
involve an inventive step

"Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art.

"Δ" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

02 OCTOBER 1990

Date of Mailing of this International Search Report

28 JAN 1991

International Searching Authority

ISA/US

Signature of Authorized Officer

Susan Berman

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